

Use of radiation-curable resins based on hydrogenated ketone-aldehyde and phenol-aldehyde resins

The invention relates to the use of radiation-curable resins based on carbonyl-hydrogenated
5 ketone-aldehyde and ring-hydrogenated phenol-aldehyde resins.

Radiation-curable coating materials have increasingly gained in importance within recent
years, for reasons including the low VOC (volatile organic compounds) content of these
systems.

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The film-forming components in the coating material are of relatively low molecular mass
and hence of low viscosity, so that there is no need for high fractions of organic solvents.
Durable coatings are obtained by the formation, following application of the coating material,
of a high molecular mass, polymeric network by means of crosslinking reactions initiated by,
15 for example, electron beams or UV light.

Hard resins such as, for example, ketone-aldehyde resins are used in coating materials, for
example, as additive resins in order to enhance certain properties such as initial drying rate,
gloss, hardness or scratch resistance. Owing to their relatively low molecular weight,
20 customary ketone-aldehyde resins possess a low melt viscosity and solution viscosity and
therefore also serve as film-forming functional fillers in coating materials.

Ketone-aldehyde resins normally possess hydroxyl groups and can therefore be crosslinked
only with, for example, polyisocyanates or amine resins. These crosslinking reactions are
25 usually initiated and/or accelerated thermally.

For radiation-initiated crosslinking reactions, in accordance with cationic and/or free-radical
reaction mechanisms, the ketone-aldehyde resins are not suitable.

30 Accordingly, the ketone-aldehyde resins are normally added to radiation-curable coating
systems as, for example, a film-forming passive, i.e., noncrosslinking component. Owing to
the uncrosslinked resin fractions, the resistance of such coatings to gasoline, chemicals or

solvents, for example, is often relatively low.

DE 23 45 624, EP 736 074, DE 28 47 796, DD 24 0318, DE 24 38 724, and JP 09143396 describe the use of ketone-aldehyde resins and ketone resins, e.g., cyclohexanone-
5 formaldehyde resins, in radiation-curable systems. Radiation-induced crosslinking reactions of these resins are not described.

EP 0 902 065 describes the use of nonradiation-curable resins formed from urea (derivatives), ketone or aldehydes as an added component in a mixture with radiation-curable resins.

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DE 24 38 712 describes radiation-curing printing inks composed of film-forming resins, ketone resins and ketone-formaldehyde resins, and polymerizable components such as polyfunctional acrylate esters of polyhydric alcohols. To the skilled worker it is obvious that radiation-induced crosslinking reaction of the modified ketone-aldehyde resins and ketone
15 resins can only come about through the use of unsaturated fatty acids. It is known, however, that resins having a higher oil content tend toward, for example, unwanted yellowing and thus their use in high-quality coatings is limited.

US 4,070,500 describes the use of nonradiation-curable ketone-formaldehyde resins as a
20 film-forming component in radiation-curable inks.

The carbonyl groups have long been converted into secondary alcohols by hydrogenation of ketone-aldehyde resins (DE-C 8 70 022). A typical and known product is Kunstharz SK from Degussa AG. Likewise known are resins on a phenolic resin basis, whose aromatic units have
25 been converted by hydrogenation into cycloaliphatic groups, with some of the hydroxyl groups being retained. The use of carbonyl- and ring-hydrogenated ketone-aldehyde resins based on ketones containing aromatic groups is likewise possible. Such a resin is described in DE 33 34 631. The OH number of such products, at more than 200 mg KOH/g, is very high.

30 It was an object of the present invention to find radiation-curable crosslinkable resins for use in coating materials, adhesives, inks, including printing inks, polishes, varnishes, pigment pastes and masterbatches, fillers, sealants and insulants and/or cosmetic articles which

produce durable and robust coatings, seals and adhesive bonds, are insoluble after crosslinking, and possess great hardness and abrasion resistance, a high gloss, and a high stability toward hydrolysis.

5 Surprisingly it has been possible to achieve this object by using carbonyl-hydrogenated ketone-aldehyde resins and/or ring-hydrogenated phenol resins containing ethylenically unsaturated moieties as a main, base or additional component in radiation-curing coating materials, adhesives, inks, including printing inks, polishes, varnishes, pigment pastes and masterbatches, fillers, sealants and insulants and/or cosmetic articles.

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It has been found that the use of the radiation-curable resins of the invention based on carbonyl-hydrogenated ketone-aldehyde resins and ring-hydrogenated phenol-aldehyde resins as a main, base or additional component in radiation-curing coating materials, adhesives, inks, including printing inks, polishes, varnishes, pigment pastes and masterbatches, fillers, sealants
15 and insulants and/or cosmetic articles brings about a reduction in viscosity, thereby making it possible very largely to omit low molecular mass constituents - particularly volatile organic solvents which may possibly also contain reactive groups (and are then known as reactive diluents) - which is desirable on environmental and toxicological grounds.

20 The use of the radiation-curable resins of the invention based on carbonyl-hydrogenated ketone-aldehyde resins and ring-hydrogenated phenol-aldehyde resins as a main, base or additional component in radiation-curing coating materials, adhesives, inks, including printing inks, polishes, varnishes, pigment pastes and masterbatches, fillers, sealants and insulants and/or cosmetic articles results in greater gloss and greater hardness and also abrasion
25 resistance, improved chemical resistance and solvent resistance, and very high stability toward hydrolysis at the same time.

Additionally there is an improvement in the adhesion to substrates such as metals, plastics, wood, paper, textiles, and glass, for example, and also mineral substrates, thereby enhancing
30 the protection afforded to these substrates, through an increase in corrosion resistance, for example. There is also an increase in the intercoat adhesion, thereby improving the adhesion of further applied coats.

Both pigment wetting and stabilization of the pigments are improved. It is possible to achieve the same color shade and color strengths with a smaller amount of pigment if the products according to the invention are used. This is particularly advantageous not least on economic grounds, since not only high-priced pigments but also additive wetting and stabilizing agents can be at least reduced.

Particular preference is given to the use of the radiation-curable resins as a main component, base component or additional component in radiation-curing fillers, primers, surfacers, base-coat, topcoat, and clearcoat materials, particularly on metals, plastics, wood, paper, textiles and glass and also on mineral substrates.

Besides the radiation-curable resins it is possible for other oligomers and/or polymers, selected from the group consisting of polyurethanes, polyesters, polyacrylates, polyolefins, natural resins, epoxy resins, silicone oils and silicone resins, amine resins, fluoro polymers, and derivatives thereof, to be present, alone or in combination. Depending on the desired properties and the nature of the application it is possible for the amount of the further oligomers and/or polymers to be between 98% and 5%.

The radiation-curable resins may also comprise auxiliaries and additives selected from inhibitors, organic solvents, with or without unsaturated moieties, surface-active substances, oxygen scavengers and/or free-radical scavengers, catalysts, light stabilizers, color brighteners, photoinitiators, photosensitizers, thixotropic agents, antiskinning agents, defoamers, dyes, pigments, fillers, and dulling agents. The amount varies greatly according to the field of use and nature of the auxiliary and additive.

The invention provides for the use of radiation-curable resins essentially comprising

- A) at least one carbonyl-hydrogenated ketone-aldehyde resin
and/or
- 30 B) at least one ring-hydrogenated phenol-aldehyde resin
and
- C) at least one compound comprising at least one ethylenically unsaturated moiety having

at the same time at least one moiety which is reactive toward A) and/or B),
as a main component, base component or additional component in radiation-curing
coating materials, adhesives, inks, including printing inks, polishes, varnishes, pigment
pastes and masterbatches, fillers, sealants and insulants and/or cosmetic articles.

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The invention also provides for the use of radiation-curable resins obtained by polymer-analogously reacting

A) at least one carbonyl-hydrogenated ketone-aldehyde resin
and/or

10 B) at least one ring-hydrogenated phenol-aldehyde resin
and

C) at least one compound comprising at least one ethylenically unsaturated moiety and at
the same time at least one moiety which is reactive toward A) and/or B),
as a main component, base component or additional component in radiation-curing
15 coating materials, adhesives, inks, including printing inks, polishes, varnishes, pigment
pastes and masterbatches, fillers, sealants and insulants and/or cosmetic articles.

The text below describes in more detail the radiation-curable resins of the invention based on
carbonyl-hydrogenated ketone-aldehyde resins and ring-hydrogenated phenol-aldehyde resins.

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Suitable ketones for preparing the carbonyl-hydrogenated ketone-aldehyde resins
(component A) include all ketones, especially acetone, acetophenone, methyl ethyl ketone,
tert-butyl methyl ketone, heptan-2-one, pentan-3-one, methyl isobutyl ketone,
cyclopentanone, cyclododecanone, mixtures of 2,2,4- and 2,4,4-trimethylcyclopentanone,
25 cycloheptanone and cyclooctanone, cyclohexanone and all alkyl-substituted cyclohexanones
having one or more alkyl radicals containing in total 1 to 8 carbon atoms, individually or in a
mixture. Examples that may be mentioned of alkyl-substituted cyclohexanones include 4-tert-
amylcyclohexanone, 2-sec-butylcyclohexanone, 2-tert-butylcyclohexanone, 4-tert-
butylcyclohexanone, 2-methylcyclohexanone, and 3,3,5-trimethylcyclohexanone.

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In general, however, any of the ketones said in the literature to be suitable for ketone resin
syntheses, more generally all C-H-acidic ketones, can be used. Preference is given to

carbonyl-hydrogenated ketone-aldehyde resins based on the ketones acetophenone, cyclohexanone, 4-tert-butylcyclohexanone, 3,3,5-trimethylcyclohexanone, and heptanone, alone or in a mixture.

- 5 Suitable aldehyde components of the carbonyl-hydrogenated ketone-aldehyde resins (component A) include in principle linear or branched aldehydes, such as formaldehyde, acetaldehyde, n-butyraldehyde and/or isobutyraldehyde, valeraldehyde, and dodecanal. In general it is possible to use any of the aldehydes said in the literature to be suitable for ketone resin syntheses. It is preferred, however, to use formaldehyde, alone or in mixtures.

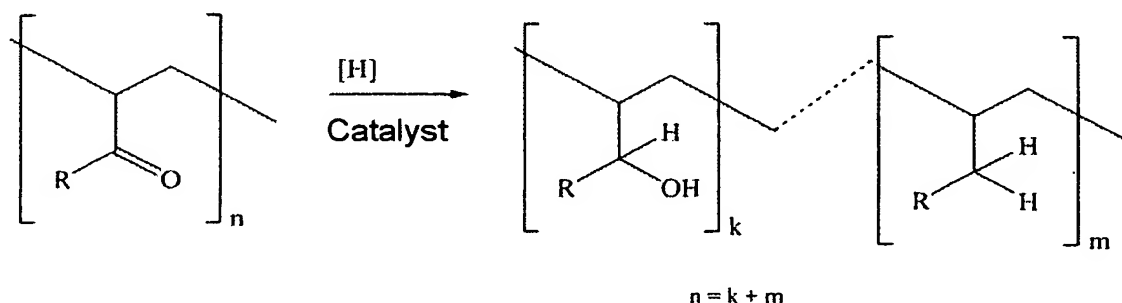
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The requisite formaldehyde is normally used in the form of an aqueous or alcoholic (e.g., methanol or butanol) solution with a strength of from about 20 to 40% by weight. Other forms of formaldehyde, such as para-formaldehyde or trioxane, for example, are likewise possible. Aromatic aldehydes, such as benzaldehyde, can likewise be present in a mixture with
15 formaldehyde.

Particularly preferred starting compounds used for the component A) carbonyl-hydrogenated resins are acetophenone, cyclohexanone, 4-tert-butylcyclohexanone, 3,3,5-trimethylcyclohexanone, and heptanone, alone or in a mixture, and formaldehyde.

20

- The resins of ketone and aldehyde are hydrogenated with hydrogen in the presence of a catalyst at pressures of up to 300 bar. In the course of the hydrogenation the carbonyl group of the ketone-aldehyde resin is converted into a secondary hydroxyl group. Depending on reaction conditions, some of the hydroxyl groups may be eliminated, resulting in methylene
25 groups. This is illustrated in the following scheme:



As component B) use is made of ring-hydrogenated phenol-aldehyde resins of the novolak type using the aldehydes such as formaldehyde, butyraldehyde or benzaldehyde, for example, preferably formaldehyde. To a minor extent it is possible to use nonhydrogenated novolaks, but these then have lower light fastnesses.

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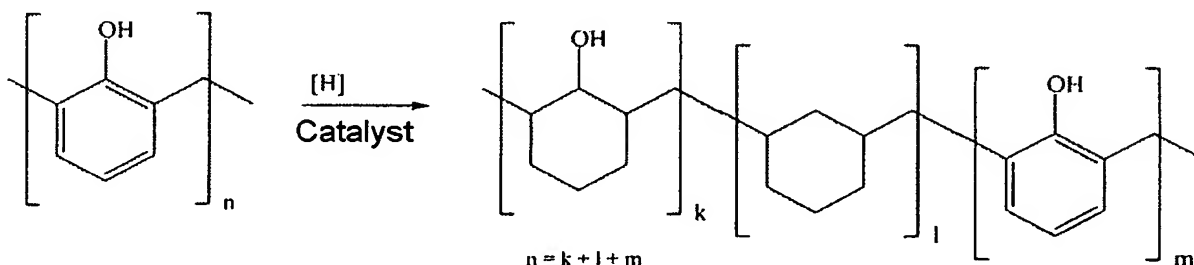
Particularly suitable are ring-hydrogenated resins based on alkyl-substituted phenols. In general it is possible to use any of the phenols said in the literature to be suitable for phenolic resin syntheses.

- 10 Examples of suitable phenols that may be mentioned include phenol, 2- and 4-tert-butylphenol, 4-amyphenol, nonylphenol, 2- and 4-tert-octylphenol, dodecylphenol, cresol, xylenols, and bisphenols. They can be used alone or in a mixture.

- 15 It is particularly preferred to use ring-hydrogenated, alkyl-substituted phenol-formaldehyde resins of the novolak type. Preferred phenolic resins are reaction products of formaldehyde and 2- and 4-tert-butylphenol, 4-amyphenol, nonylphenol, 2- and 4-tert-octylphenol, and dodecylphenol.

- 20 The novolaks are hydrogenated with hydrogen in the presence of a suitable catalyst. Through the choice of the catalyst the aromatic ring is converted into a cycloaliphatic ring. Through a suitable choice of the parameters the hydroxyl group are retained.

This is illustrated by the following scheme:



- 25 Through the choice of the hydrogenation conditions it is also possible for the hydroxyl groups to be hydrogenated, thereby giving rise to cycloaliphatic rings. The ring-hydrogenated resins

possess OH numbers of from 50 to 450 mg KOH/g, preferably from 100 to 350 mg KOH/g, more preferably from 150 to 300 mg KOH/g. The fraction of aromatic groups is below 50% by weight, preferably below 30% by weight, more preferably below 10% by weight.

- 5 The radiation-curable resins on which the invention is based are obtained by polymer-analogous reaction of the hydrogenated ketone-aldehyde resins and/or of the phenol-aldehyde resins, in the melt or in a suitable solvent solution, with component C). Suitability as component C) is possessed by maleic anhydride, (meth)acrylic acid derivatives such as (meth)acryloyl chloride, glycidyl (meth)acrylate, (meth)acrylic acid and/or the low molecular
- 10 mass alkyl esters and/or anhydrides thereof, alone or in a mixture. It is also possible to obtain radiation-curable resins by reacting the hydrogenated ketone-aldehyde resins and phenol-aldehyde resins with isocyanates possessing an ethylenically unsaturated moiety, such as (meth)acryloyl isocyanate, α,α -dimethyl-3-isopropenylbenzyl isocyanate, (meth)acryloylalkyl isocyanate with alkyl spacers possessing from 1 to 12, preferably from 2 to 8, more preferably
- 15 from 2 to 6 carbon atoms, such as methacryloyl ethyl isocyanate and methacryloyl butyl isocyanate, for example. Further reaction products which have proven suitable are those of hydroxyalkyl (meth)acrylates whose alkyl spacers have from 1 to 12, preferably from 2 to 8, more preferably from 2 to 6 carbon atoms and diisocyanates such as, for example, cyclohexane diisocyanate, methylcyclohexane diisocyanate, ethylcyclohexane diisocyanate,
- 20 propylcyclohexane diisocyanate, methyldiethylcyclohexane diisocyanate, phenylene diisocyanate, tolylene diisocyanate, bis(isocyanatophenyl)methane, propane diisocyanate, butane diisocyanate, pentane diisocyanate, hexane diisocyanate, such as hexamethylene diisocyanate (HDI) or 1,5-diisocyanato-2-methylpentane (MPDI), heptane diisocyanate, octane diisocyanate, nonane diisocyanate, such as 1,6-diisocyanato-2,4,4-trimethylhexane or
- 25 1,6-diisocyanato-2,2,4-trimethylhexane (TMDI), nonane triisocyanate, such as 4-isocyanatomethyloctane 1,8-diisocyanate (TIN), decane di- and triisocyanate, undecane di- and triisocyanate, dodecane di- and triisocyanates, isophorone diisocyanate (IPDI), bis(isocyanatomethylcyclohexyl)methane (H_{12} MDI), isocyanatomethylmethylcyclohexyl isocyanate, 2,5(2,6)-bis(isocyanatomethyl)bicyclo[2.2.1]heptane (NBDI), 1,3-bis(iso-
- 30 cyanatomethyl)cyclohexane (1,3- H_6 -XDI) or 1,4-bis(isocyanatomethyl)cyclohexane (1,4- H_6 -XDI), alone or in a mixture. Examples that may be mentioned include the reaction products in a 1:1 molar ratio of hydroxyethyl acrylate and/or hydroxyethyl methacrylate with isophorone

diisocyanate and/or H₁₂MDI and/or HDI.

Another preferred class of polyisocyanates are the compounds having more than two isocyanate groups per molecule which are prepared by trimerizing, allophanatizing, biuretizing and/or urethaneizing the simple diisocyanates, examples being the reaction products of these simple diisocyanates, such as IPDI, HDI and/or H₁₂MDI, for example, with polyhydric alcohols (e.g., glycerol, trimethylolpropane, pentaerythritol) and/or polyfunctional polyamines or else the triisocyanurates obtainable by trimerizing the simple diisocyanates, such as IPDI, HDI, and H₁₂MDI, for example.

If desired it is possible to use a suitable catalyst for preparing the resins of the invention. Suitable compounds are all those known in the literature which accelerate an OH-NCO reaction, such as diazabicyclooctane (DABCO) or dibutyltin dilaurate (DBTL) for example.

The functionality of the resins obtained ranges from low to high in accordance with the ratio of the reactants to one another. Through the choice of reactants it is also possible to set the subsequent hardness of the crosslinked film. If, for example, a hard resin such as hydrogenated-formaldehyde resin is reacted with α,α -dimethyl-3-isopropenylbenzyl isocyanate, the resulting products are harder than those obtained through the use of (meth)acryloyl ethyl isocyanate and/or hydroxyethyl acrylate-isophorone diisocyanate adducts; the flexibility, however, is then lower. It has also been found that the reactivity of ethylenically unsaturated compounds with little steric hindrance - such as of hydroxyethyl acrylate, for example - is higher than in the case of those which are sterically hindered, such as α,α -dimethyl-3-isopropenylbenzyl isocyanate, for example.

It is also possible to replace some of the carbonyl-hydrogenated ketone-aldehyde resins A) and/or ring-hydrogenated phenol-aldehyde resins B) by further hydroxy-functionalized polymers such as hydroxy-functional polyethers, polyesters and/or polyacrylates, for example. In this case, mixtures of these polymers with the ketone-aldehyde resins and/or phenol-aldehyde resins can be reacted polymer-analogously with component C). It has been found that first of all it is also possible to prepare adducts of the ketone-aldehyde resins and/or phenol-aldehyde resins with, for example, hydroxy-functional polyethers, polyesters and/or

polyacrylates using the abovementioned diisocyanates and/or triisocyanates, and only then are these adducts reacted polymer-analogously with component C). In contrast to the "plain" carbonyl-hydrogenated ketone-aldehyde resins and/or ring-hydrogenated phenol-aldehyde resins it is possible by this means better to set properties such as flexibility and hardness, for
5 example. The further hydroxy-functional polymers generally possess molecular weights M_n of between 200 and 10 000 g/mol, preferably between 300 and 5 000 g/mol.

The resins on which the invention is based are prepared in the melt or in a suitable, organic solvent solution of the carbonyl-hydrogenated ketone-aldehyde resins and/or ring-
10 hydrogenated phenol-aldehyde resins.

Said organic solvent may if desired likewise possess unsaturated moieties, in which case it acts directly as a reactive diluent in the subsequent application.

For this purpose, in one preferred embodiment I,
15 the compound comprising at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and/or B), in the presence if desired of a suitable catalyst, is added to the solution or melt of the carbonyl-hydrogenated ketone-aldehyde resin A) and/or ring-hydrogenated phenol-aldehyde resin B).

20 The temperature of the reaction is selected in accordance with the reactivity of component C). Where isocyanates are used as component C), suitable temperatures have been found to be between 30 and 150°C, preferably between 50 and 140°C.

The solvent that may be present can be separated off if desired after the end of the reaction, in
25 which case a powder of the product of the invention is generally obtained.

It has proven advantageous to react 1 mol of the carbonyl-hydrogenated ketone-aldehyde resin and/or ring-hydrogenated phenol-aldehyde resin - based on M_n - with from 0.5 to 15 mol, preferably from 1 to 10 mol, in particular from 2 to 8 mol of the unsaturated
30 compound (component C).

In a preferred embodiment II

the compound comprising at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and/or B) and the additional polymer, in the presence if desired of a suitable catalyst, is added to the solution or melt of the carbonyl-hydrogenated ketone-aldehyde resin A) and/or ring-hydrogenated phenol-aldehyde resin B) and the hydroxy-functional polymer, such as polyether, polyester and/or polyacrylate, for example.

The temperature of the reaction is selected in accordance with the reactivity of component C). Where isocyanates are used as component C), suitable temperatures have been found to be between 30 and 150°C, preferably between 50 and 140°C.

The solvent that may be present can be separated off if desired after the end of the reaction, in which case a powder of the product of the invention is generally obtained.

It has proven advantageous to react 1 mol of the carbonyl-hydrogenated ketone-aldehyde resins and/or ring-hydrogenated-phenol-aldehyde resins and/or additional polymers - based on M_n - with from 0.5 to 15 mol, preferably from 1 to 10 mol, in particular from 2 to 8 mol of the unsaturated compound (component C).

In a preferred embodiment III

a di- and/or trifunctional isocyanate is added to the solution or melt of the carbonyl-hydrogenated ketone-aldehyde resin A) and/or ring-hydrogenated phenol-aldehyde resin B) and the hydroxy-functional polymer, such as polyether, polyester and/or polyacrylate, for example, and a hydroxy-functional preadduct is prepared. Only then is the compound comprising at least one ethylenically unsaturated moiety and at the same time at least one moiety which is reactive toward A) and/or B) and the additional polymer, in the presence if desired of a suitable catalyst, added.

The temperature of the reaction is selected in accordance with the reactivity of component C). Where isocyanates are used as component C), suitable temperatures have been found to be between 30 and 150°C, preferably between 50 and 140°C.

The solvent that may be present can be separated off if desired after the end of the reaction, in which case a powder of the product of the invention is generally obtained.

It has proven advantageous to react 1 mol of component A) and/or component B) and/or additional polymers - based on M_n - with from 0.5 to 15 mol, preferably from 1 to 10 mol, in particular from 2 to 8 mol of the unsaturated compound (component C).

In the presence of suitable photoinitiators, and in the presence if desired of suitable photosensitizers, these resins can be converted by irradiation into polymeric, insoluble networks which, depending on the level of ethylenically unsaturated groups present, produce elastomers to thermosets.

The examples which follow are intended to illustrate the invention made but not to restrict its scope of application:

Example 1 (UV 17):

Synthesis takes place by reaction of 1 mol of Kunstharz SK (Degussa AG; hydrogenated resin formed from acetophenone and formaldehyde; OHN = 240 mg KOH/g (acetic anhydride method), $M_n \sim 1000$ g/mol) with 1.5 mol of a reaction product of IPDI and hydroxyethyl acrylate in a ratio of 1:1 in the presence of 0.2% (on resin) of 2,6-bis(tert-butyl)-4-methylphenol (Ralox BHT, Degussa AG) and 0.1% (on resin) of dibutyltin dilaurate, 65% strength in methoxypropyl acetate, at 80°C under nitrogen in a three-necked flask with stirrer, reflux condenser, and temperature sensor until an NCO number of less than 0.1 is reached. The pale, clear solution obtained possesses a dynamic viscosity of 51.56 Pa·s.

Example 2 (UV 19):

The reaction is carried out of 1 mol of Kunstharz SK (Degussa AG; OHN = 240 mg KOH/g (acetic anhydride method), $M_n \sim 1000$ g/mol) and 4 mol of a reaction product of IPDI and hydroxyethyl acrylate in a ratio of 1:1 in the presence of 0.2% (on resin) of 2,6-bis(tert-butyl)-4-methylphenol (Degussa AG) and 0.1% (on resin) of dibutyltin dilaurate, 65% strength in methoxypropyl acetate, at 80°C under nitrogen in a three-necked flask with stirrer, reflux condenser, and temperature sensor until an NCO number of less than 0.1 is reached. The pale, clear solution obtained possesses a dynamic viscosity of 26.2 Pa·s.

Use examples

The base resin (UV 20) used was an adduct of trimethylolpropane, IPDI, Terathane 650 and hydroxyethyl acrylate, as a 70% strength solution in MOP acetate, viscosity at 23°C = 19.2 Pas.

Also investigated, for comparison, was the physically admixed, noncrosslinking Kunstharz SK.

Viscosities of the different systems in 50% form in MOP acetate without photoinitiator

Number	Mixing ratio solids	Dyn. viscosity 23°C
Single-substance systems		
481	A-UV 20	775 mPas
478	A-UV 17	430 mPas
480	A-UV 19	370 mPas
Mixtures		
494	A-UV 20 : Kunstharz SK = 95 : 5	760 mPas
495	A-UV 20 : Kunstharz SK = 90 : 10	750 mPas
482	A-UV 20 : A-UV 17 = 95 : 5	740 mPas
483	A-UV 20 : A-UV 17 = 90 : 10	720 mPas
484	A-UV 20 : A-UV 17 = 80 : 20	670 mPas
488	A-UV 20 : A-UV 19 = 95 : 5	750 mPas
489	A-UV 20 : A-UV 19 = 90 : 10	710 mPas
490	A-UV 20 : A-UV 19 = 80 : 20	650 mPas

As the proportion of the products of the invention goes up there is a fall in the dynamic viscosity of the formulations.

Summary of the coatings data obtained

Darocure 1173 (for amount see table) was added to the mixtures and they were drawn down onto metal panels using a doctor blade. The systems contain solvent; therefore initial drying was carried out in a forced-air oven at 80°C for 30 minutes. The films were then cured by means of UV light (medium-pressure mercury lamp, 70 W/optical filter 350 nm) (3×6 s).

Coating No.	Resin mix. based on resin	1173 [% based on resin]	NVC [%]	UV- curing Mini-Cure	Coatings data								
					FT μ	CH / Tesa	HB	EC	HK	BI	Peugeot test	MEK test	Flow
481	A-UV 20 Standard	1.50	50.4	6"	n.m. too soft, sticks readily								minimally restless surf.
				2 x 6"	31-39	2B / 5B	n.m.	n.m.	38	>80 dir >80 rev	o	>150 ++	
				3 x 6"	30-39	1B / 5B	n.m.	n.m.	53	>80 dir >80 rev	o/+	>150 ++	
481 B	A-UV 20	3.00	50.7	6"	n.m. sticks readily					46			minimally restless surf.
				2 x 6"	28-36	5B	71	10	48	>80	o	>150++	
				3 x 6"	30-38	5B	67	>9	45	>80	o	>150++	
478	A-UV 17	1.50	50.4	6"	32-38	5B	n.m.	<0.5	192	<10	++	39	slightly restless surf.
				2 x 6"	32-42	4-5B / 5B	n.m.	<0.5	201	<10	++	64	
				3 x 6"	33-47	4-5B / 5B	111	<0.5	203	<10	++	140	
480	A-UV 19	1.50	50.4	6"	35-38	4-5B / 5B	n.m.	<0.5	194	<10	++	120	slightly restless surf.
				2 x 6"	35-38	4-5B / 5B	143	<0.5	202	<10	++	>150++	
				3 x 6"	34-39	4-5B / 5B	143	<0.5	200	<10	++	>150++	
494	A-UV 20 95 Kunsth. SK 5	1.50	50.4	3 x 6"	28-33	0-1B / 5B	71	9 / >9.5	48	>80	o/+	>150 o	minimally restless surf.
495	A-UV 20 90 Kunsth. SK 10	1.50	50.4	3 x 6"	30-38	0B / 5B	71	9 / >9.5	59	>80	o/+	>150 (135) ++	minimally restless surf.

1173 : Darocur 1173

- Physical admixing of the unsubstituted resins already improves hardness, adhesion and the
- 5 Peugeot and MEK tests. Mechanical properties, as can be determined by the impact test and Erichsen cupping, are impaired, however.

Coating No.	Resin mix. based on resin	1173 [% based on resin]	NVC [%]	UV- curing Mini-Cure	FT μ	Coatings data								Flow
						CH / Tesa	HB	EC	HK	BI	Peugeot test	MEK test		
482	A-UV 20 95 A-UV 17 5	1.50	50.4	3 x 6"	30-37	0-1B / 5B	71	9	78	>80	++	>150 o/+	slightly restless surf.	
483	A-UV 20 90 A-UV 17 10	1.50	50.4	3 x 6"	30-33	0B / 5B	77	10	101	>80	++	>150 +/++	minimally restless surf.	
				3 x 6"	31-33	Film removed from glass prior to measurement								
484	A-UV 20 80 A-UV 17 20	1.50	50.4	3 x 6"	30-36	0-1B / 5B	91	8.5/ 9	146	>80	++	>150 +/++	okay	
				3 x 6"	31-32	Film removed from glass prior to measurement								
488	A-UV 20 95 A-UV 19 5	1.50	50.4	3 x 6"	31-38	0-1B / 5B	71	10	66	>80	o/+	>150 ++	minimally restless surf.	
489	A-UV 20 90 A-UV 19 10	1.50	50.4	3 x 6"	28-38	0B / 5B	77	9.5	84	>80	o/+	>150 ++	minimally restless surf.	
				3 x 6"	29-37	0-1B / 5B	83	9 >9.5	75	>80	o	>150(121) ++		
490	A-UV 20 80 A-UV 19 20	1.50	50.4	3 x 6"	32-38	1-2B / 5B	91	7.5/ 7	147	>80	++	>150/--	minimally restless surf.	

1173 : Darocur 1173

Chemical crosslinking of the products of the invention with the clear coating material increases the hardness and the adhesion. The premium-grade gasoline resistance (Peugeot test) and solvent resistance (MEK test) are likewise improved. Mechanical properties which were impaired in the case of the purely physical admixtures are likewise improved, which is manifested in good values for impact test and Erichsen cupping.

Yellowness index

The investigations were made on the free film. Darocur 1173 was added to the mixtures and then drawn down onto glass, dried at 80°C for 30 minutes, and irradiated three times for 6 s. The base line Y_i value of the substrate is 0.08.

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Coating No.	Resins	Synthetic resin content	FT	Yi values			
	Solids	[% based on resin]	μ	Initial	1h 120°C	1h 160°C	1h 200°C
Blending with plain synthetic resins							
481	A-UV 20	-	31-32	0.4	0.4	1.7	50.4 24-27 μ
494	A-UV 20 95 Kunsth. SK 5	5.0	31-34	0.2	0.3	2.7	40.4
495	A-UV 20 90 Kunsth. SK 10	10.0	31-34	0.3	0.4	1.7	36.3
Blending with synthetic resin A adduct							
482	A-UV 20 95 A-UV 17 5	3.0	30-32	0.2	0.4	1.2	44.6 25-28 μ
483	A-UV 20 90 A-UV 17 10	5.9	31-33	0.5	0.5	2	38 27-31 μ
484	A-UV 20 80 A-UV 17 20	11.8	31-32	0.2	0.5	2.5	28.6
488	A-UV 20 95 A-UV 19 5	1.8	30-32	0.2	0.3	1.6 28-31 μ	40.4 27-30 μ
489	A-UV 20 90 A-UV 19 10	3.5	30-32	0.2	0.3	2.5	42.2 26-29 μ
490	A-UV 20 80 A-UV 19 20	7.0	30-32	0.2	0.3	2.2	33.5 28-30 μ

B = twice the amount of Darocur 1173 (see coatings data)

The yellowing tendency is improved as compared with the standard system, particularly in the case of exposure to high temperatures.

Abbreviations

- DBTL: dibutyltin dilaurate
EC: Erichsen cupping
HB: Buchholz hardness
5 HK: König pendulum hardness
IPDI: isophorone diisocyanate
BI: ball impact
MEK test: resistance to butanone
MOP acetate: methoxypropyl acetate
10 NVC: nonvolatile constituents
Peugeot test: premium-grade gasoline resistance
FT: film thickness